

The University of Chicago

I. A TEMPERATURE VARIATION METHOD TO ASSIST
IN VIBRATIONAL ANALYSES OF COMPLEX
MOLECULAR SPECTRA

II. ON THE ABSORPTION SPECTRUM OF SULPHUR
DIOXIDE

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE PHYS-
ICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1935

By

JOHN HERBERT CLEMENTS

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A Temperature Variation Method to Assist in Vibrational Analyses of Complex Molecular Spectra

J. H. CLEMENTS, *University of Chicago*

(Received December 7, 1934)

A temperature variation method of determining the initial (lower) vibrational levels of the absorption bands of an electronic band system of a polyatomic molecule is presented. The determination is made from photometric measurements of the absorption at two temperatures not widely separated. Such absorption tube lengths are used that the absorption is everywhere much less than 100 percent in the bands to be studied. That variations in total absorption for a band may be measurable, the method is restricted to spectra in which the rotation lines are fairly broad compared with the intervals between them or else are very closely spaced. In such cases the rotational structure is blotted out on the photographic plate by the lack of resolution of the spectrograph and the exponential

absorption law may be assumed in comparing absorption intensities at the two temperatures. A criterion is laid down for the applicability of the method in any instance. An equation is developed to give the heights (in cm^{-1}) of the excited vibrational levels of the normal electronic state involved in the various transitions, above that of some arbitrarily selected band of a group, as follows:

$$\log_{10} \rho_b/\rho_a = -0.623 \left(\frac{1}{T_2} - \frac{1}{T_1} \right) (G_b - G_a)'',$$

The determination of the heights $(G_b - G_a)''$ in cm^{-1} comes from the two absolute temperatures and the ratio ρ_b/ρ_a of the heights of the absorption peaks on the two microphotometer traces.

INTRODUCTION

IN the literature casual mention of the use of temperature variation to assist in the analysis of complex molecular absorption spectra is often found. The information that certain bands are associated with transitions from the normal state, while others occur from excited states whose heights above the normal state may be more or less closely estimated, may well bring order into an otherwise hopeless maze of frequencies. This information can be obtained from a systematic comparison of the relative changes in intensities of absorption of the different bands with temperature. A simple procedure applicable to a vibrational analysis in the photographic range will be presented here. The method is designed for use with closely spaced rotational structures appearing as unresolved band envelopes on the spectrum photograph. Its application could be extended to include molecules whose rotational structure can be blotted out by pressure.

The procedure is to seal off an appropriate mass of gas in an absorption tube and take plates of the absorption at two temperatures not widely separated. An extension is readily made to the investigation of a gas that dissociates under the energy of the continuous light source and must be flowed through the absorption chamber. To keep the same number of molecules in the light path under the two temperatures requires in this

case an adjustment of pressure in conformity with the gas laws. The gas can be heated before admission to the tube and the pressure can be regulated by the valves controlling its rate of admission and exhaustion.

CRITERION OF APPLICABILITY OF THE METHOD

With N absorbing molecules in the light path, we have for gas absorption the exponential law

$$I = I_0 e^{-\mu(\nu)N},$$

where $\mu(\nu)$ is the absorption coefficient of the material per molecule for frequency ν ; I is the intensity of light of frequency ν transmitted by the gas and I_0 that incident on the gas chamber. This is the law for the ideal case of a single frequency under perfect resolution. But the absorption intensity of a line M is defined as $\alpha_M = \int_M \mu(\nu) d\nu$, and moreover plates of polyatomic vibration-rotation bands usually consist of partially resolved rotation lines. Under relatively high dispersion the rotational structure may be partially distinguishable while with low dispersion instruments only an envelope of unresolved structure is observed. In either event, since the absorption coefficient of the gas varies greatly in a very small frequency range among the band lines, the limits of usefulness of the exponential law must be examined.

In the spectrum of HCL, for example, in which the band lines are narrow compared with the intervals between them, this law cannot be expected to hold in gross. In infrared work Bourgin¹ showed that it is inapplicable to a single band line directly under ordinary working conditions. The apparent failure of the law was accounted for on the basis that the resolving power of the spectrometer with the slit widths used was not sufficient to give the true shapes of the absorption curves. In the type of spectrum for which the present method is proposed, namely, for closely spaced rotational lines, the slit width is large enough to include a number of lines. Thus much overlapping occurs on the spectrum photograph and the shapes of the individual absorption lines are completely blotted out. If the overlapping is sufficient the exponential law may now hold in gross, at least the gross effects may be comparable at two temperatures relatively close together.

If the rotation lines are broad compared with the distances between them, a small change of temperature will produce a measurable change in the intensity of absorption of the apparent band envelopes. Further, under such temperature variation the shapes of the rotation lines, hence of the envelope resulting from the overlapping, should not be sensibly altered provided the slit width remains the same. If the exponential absorption law is to be applicable, it is clear that the absorptions at all positions of maximum absorption coefficient, that is at the centers of the band lines, must be kept small compared with 100 percent (Dennison²). The validity of its application is subject to experimental check in any given case. Keeping the temperature constant, the absorption tube may be filled with the gas at two pressures such that the amounts of absorption are about the same as in the two spectrum photographs in which the temperature is varied. The criterion of applicability of the method is then that the heights of all peaks on the two microphotometer traces corresponding to the two pressures shall be proportional to these pressures.

When this criterion is obeyed, the necessity of

using the technique employed by Bartholomé³ (namely, broadening the band lines under pressure until little trace of the original structure remains) is avoided. It seems then that if the band lines either are naturally broad and diffuse or if they are so closely packed that the intervals between them are small the required conditions are fulfilled. This situation has apparently been encountered in the spectrum of sulphur dioxide (see paper following). It is to be expected that this will also be the case for a number of polyatomic molecules, while with other molecules the application of moderate pressure to the gas may make the absorption amenable to the criterion for the validity of the exponential absorption law.

THE PHOTOGRAPHIC PLATE AND THE MICROPHOTOMETER

The theory of the method, involving the use of the microphotometer, will now be developed. The photographic plate, which is the basic element in the process, is discussed in a number of places.⁴ "Density" may be represented on the straight line portion of a characteristic curve for a plate by

$$D = \gamma(\log_{10} E - \log_{10} i),$$

where γ is the "contrast factor," E (exposure) is the product It^s (I =intensity, t =time of exposure and s is the Schwarzschild constant), i is the "inertia" of the plate.

To write the density numerically it is necessary to find the ratio of two blackenings. By definition $D = \log (J_0/J)$, where J_0/J is the ratio of light coming through an unblackened part of the plate to that coming through the point under consideration. The microphotometer allows this evaluation. Fig. 1 is shown as illustration. The deflection of the galvanometer of the microphotometer, a , corresponding to an unblackened part of the plate, and the null deflection, i.e., the case of no light reaching the thermo-element, are marked, respectively, as A and D . The de-

³ E. Bartholomé, *Zeits. f. physik. Chemie* **B23**, 131 (1933).

⁴ G. R. Harrison, *J. O. S. A.* **19**, 267 (1929); L. S. Ornstein, W. J. Moll and H. C. Burger, *Objektive Spektralphotometrie* (Vieweg 1932); C. E. K. Mees, *J. O. S. A.* **21**, 573 (1931).

¹ D. C. Bourgin, *Phys. Rev.* **29**, 794 (1927).

² D. M. Dennison, *Phys. Rev.* **31**, 503 (1928).

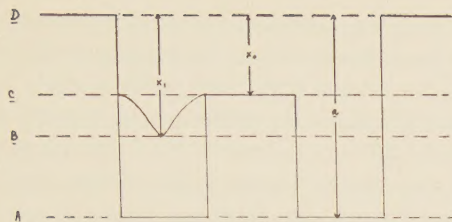


FIG. 1. A. Unblackened plate, i.e., complete absorption by gas. B. Partial absorption. C. Blackening by actual light source (no gas absorption). D. Complete blackening of photographic plate.

flections x_0 , corresponding to the continuous source, and x_1 , associated with a partial absorption, are shown at C and B, respectively. It may be assumed that small galvanometer deflections are proportional to the intensities of light incident on the thermopile of the microphotometer. Hence $J_0/J = a/x_0$ for the negative blackened by unabsorbed radiation from the continuous source, and $J_0/J = a/x$ for an adjacent region where the light of corresponding frequency has suffered selective partial absorption in a gas chamber.

Applying the exponential absorption law, which has been considered in the preceding section, for zero gas absorption we have

$$D_0 = \gamma(\log I_0 t^s - \log i) = \log(a/x_0);$$

for some gas absorption

$$D = \gamma(\log I t^s - \log i) = \log(a/x).$$

Expanding D and substituting for $\log I_0$, we get

$$\mu(\nu)N = (1/0.43\gamma) \log(x/x_0),$$

provided x and x_0 both correspond to the straight line portion of the characteristic curve. The relation is not valid when x approaches complete absorption nor when x_0 is too small resulting from overexposure of the continuous source.

What is desired is to compare $N_\nu \mu(\nu)$ for two different ν 's having in general a different number of absorbing molecules N_ν , where N_ν varies with temperature. For the frequencies ν_1, ν_2

$$(\mu N)_{\nu_2}/(\mu N)_{\nu_1} = \log(x_2/x_0)/\log(x_1/x_0).$$

If ν_1 and ν_2 show fairly weak absorption so that x_2/x_0 and x_1/x_0 are both not much greater than unity** then approximately

$$(\mu N)_{\nu_2}/(\mu N)_{\nu_1} = (x_2 - x_0)/(x_1 - x_0) = \rho.$$

If the temperature is varied by amounts which are small compared with the absolute temperature, the approximation is allowable.

POPULATION CONSIDERATIONS

Having seen the expression for the ratio of the absorption coefficients for two frequencies, now let us see what relation holds for a band envelope absorption at two temperatures. The relative absorptions of band lines depend on the relative populations of their initial states and on relative transition probabilities. The populations of the various states are given by the distribution law

$$N_1 = (p_1/p_0)N_0 e^{-G_{hc}/kT},$$

where N_0 is the number of molecules in the normal state and G is the energy in cm^{-1} of the state whose population N_1 is under consideration; p_0 and p_1 are the statistical weights, respectively. In the case that all vibrational levels are non-degenerate (as, e.g., with non-linear triatomic molecules), and if we are dealing with unresolved bands, so that N_0, N_1 stand for the total numbers of molecules in all the rotational levels of a given vibrational level, we may put $p_1 = p_0$. Changes of N_1 with temperature allow the evaluation of G , and the problem is to determine these changes from the observed changes in intensity of absorption of the vibration bands.

Curtis and Darbyshire⁵ in their work on the vibrational levels of the ICl molecule call attention to the importance of the changes of N_0 with temperature, which change had been neglected by previous workers. To avoid this difficulty they worked at constant pressure and arranged conditions to obtain equality of absorption for a particular band progression at two temperatures using the change of vapor density with temperature. In the present method this matter is taken care of in the computation rather than by an experimental procedure and so avoids the difficulties of adjustment associated with a null method. For in general comparing the intensities of two bands with initial states of energy (in cm^{-1}) G_a'' and G_b'' , respectively, at the

** In the expansion $e^y = 1 + y + \dots$, if $y < 1$, then $\log e^y = e^y - 1$, approximately.

⁵ W. E. Curtis and O. Darbyshire, Trans. Faraday Soc. 27, 77 (1931).

absolute temperatures T_1 and T_2 , we have

$$R_a^{(1)} = N_a^{(T_1)} / N_0^{(T_1)} = e^{-G_a'' h c / k T_1},$$

$$R_a^{(2)} = e^{-G_a'' h c / k T_2},$$

$$R_b^{(1)} = e^{-G_b'' h c / k T_1}, \quad R_b^{(2)} = e^{-G_b'' h c / k T_2}.$$

Let G_b'' be greater than G_a'' and T_2 greater than T_1 . The heights of the absorption peaks will be represented by $x_a^{(T_1)}$, $x_a^{(T_2)}$, $x_b^{(T_1)}$, $x_b^{(T_2)}$ and the backgrounds corresponding to zero absorption of the continuous source $x_0^{(T_1)}$, $x_0^{(T_2)}$. The differences $x_a^{(T_1)} - x_0^{(T_1)}$, etc., are proportional then to the relative numbers of absorbing molecules.

$$\frac{R_a^{(2)}}{R_a^{(1)}} = \frac{x_a^{(T_2)} - x_0^{(T_2)}}{x_a^{(T_1)} - x_0^{(T_1)}} = \rho_a = e^{-(G_a'' h c / k)(1/T_2 - 1/T_1)},$$

$$\frac{R_b^{(2)}}{R_b^{(1)}} = \rho_b = e^{-(G_b'' h c / k)(1/T_2 - 1/T_1)},$$

$$\text{or} \quad \rho_b / \rho_a = e^{-(h c / k)(1/T_2 - 1/T_1)(G_b - G_a)''},$$

$$\log_{10} \rho_b / \rho_a = -0.623(1/T_2 - 1/T_1)(G_b - G_a)''. \quad (1)$$

That is, the differences of energy (in cm^{-1}) of the initial levels of the bands appear, so that the method may be applied to a group of bands at a time. Of the group, one is arbitrarily chosen for reference and the differences in energies between the initial levels of the other bands and that of the fiducial band can be computed. This is particularly valuable in studying bands coming from the higher initial levels, where the populations fall off rapidly with vibrational quantum number so that only part of the band system appears favorably on the photograph for a given pressure of gas in the absorption chamber. It is also convenient if a prism spectrograph with changing dispersion is used. Corrections between bands in different groups can then be determined by using exposures showing overlapping of adjoining groups. The case $G_a'' = 0$ is an important special case in the above.

PRACTICAL CONSIDERATIONS

Some fluctuation of the continuous source obviously is not of serious consequence in the two temperature pictures if the exposures are taken on the same plate and developed together with constant rocking. This procedure ensures

that γ may be cancelled out in the computation as has been done above. According to Mees,⁴ γ should be about $0.8\gamma_\infty$ for photometric work. For the galvanometer of the microphotometer to give large differences in deflection, the plate must not be very dense. Hence a shorter exposure and more prolonged development than is usual in spectroscopic work is indicated. Of course all plate blackenings must be on the straight part of the characteristic curve. Plates of medium speed are the most suitable giving a balance among latitude, contrast, speed and grain.

A small disturbance of the optical system between the two temperature exposures also does not invalidate the results obtained from the equation developed, inasmuch as a ratio of peak heights on the microphotometer traces is used. Likewise if between runs the microphotometer lamp changes slightly no serious damage is done although the lamp must remain constant during the course of any single run. However, if a long absorption tube is used, the light beam in the tube should be well collimated, since otherwise the change of refractive index of the gas with temperature will alter the cone of light so that the two plates may be of considerably different density. The optical arrangement may consist of a point source and an achromatic lens, or in the ultraviolet a long small bore hydrogen discharge tube used without a lens and with shields to limit the beam is quite satisfactory. If the intensity is sufficient, it is convenient to use no lens to focus the light emerging from the absorption chamber on the slit of the spectrograph; if the light must be conserved an achromatic lens may be inserted to converge, but not focus it, in order that the spectrum shall be uniform across the slit.

Unfortunately in general the formula cannot be applied in a simple way over the whole band system due to overlapping of bands. In polyatomic spectra the complication that the band envelopes under investigation are the resultants of more or less closely overlapping vibration-rotation bands is common. Under this condition the ratios of intensities found for the absorption peaks will give apparent values of $(G_b - G_a)''$ as intermediate values which will depend on the relative strengths of the overlapping components. Nevertheless in some part of the spectrum a

group of more or less unmixed peaks is likely to be found giving a clue to the proper assignment of the bands. Then the intermediate values of $(G_b - G_a)''$ serve as intensity checks on a proposed analysis.

If there exists a background of absorption from many unresolved weak bands or a continuous background which suffers temperature variation,

only an examination leading to qualitative results may be feasible. Under such circumstances the line from which peak heights in the traces are measured (x_0) will have to be drawn from an appraisal of the condition present.

The writer wishes to thank Professor R. S. Mulliken for many consultations during the development of this discussion.

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On the Absorption Spectrum of Sulphur Dioxide

J. H. CLEMENTS, *University of Chicago*

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An attempt to organize the absorption bands of sulphur dioxide in the region 3900–2600 Å has been made. The $(000)'' - (000)'$ transition $\lambda 3129.5 \text{ Å}$ ($31,945 \text{ cm}^{-1}$) has been definitely located from a study of the temperature behavior of the lower frequency bands. Two of the vibrational frequencies known in the normal state have been observed and the intervals between successive lower levels determined. One of the frequencies in the excited state has been definitely assigned and a tentative value has been assigned for a second frequency. The configuration of the excited molecule is discussed.

INTRODUCTION

THE spectrum of sulphur dioxide, a molecule known from its permanent dipole moment to be of triangular form¹ has attracted much attention. The normal modes of vibration of this type of molecule are well known.² If, as is very likely true of SO_2 , the strong forces are those binding two atoms (here O) to a central atom (here S), the three frequencies can be classified as ν_2 , a "deformation" frequency and ν_1 and ν_3 , the symmetrical and unsymmetrical "valence" frequencies. The normal state of sulphur dioxide has been investigated from infrared and Raman data and the frequencies of the normal vibrations established with some certainty.³

Bands involving electronic transitions occur in the ultraviolet region of the spectrum and have been recognized as jumps to more than one excited electronic state. The more intensely absorbing higher frequency band system has been examined in emission and absorption by

Chow,⁴ in absorption by Jonescu⁵ and at still higher frequencies by Wieland.⁶ The lower frequency region, which is the subject of the present communication, has already been studied by Watson and Parker,⁷ who arranged some of the observed absorption bands into series. These workers however used the older frequency for the ν_2 vibration of the molecule in the normal state; also they followed the formula for a diatomic molecule separately for the three modes of vibration, as has been pointed out by Dutta.⁸ It thus seemed desirable to reexamine this portion of the spectrum. As a result of the present work, the $(0, 0, 0)'' - (0, 0, 0)'$ band** has been located through detailed study of the temperature behavior of the various bands, using photo-

⁴ T. C. Chow, *Phys. Rev.* **44**, 638 (1933).

⁵ A. Jonescu, *Comptes rendus* **197**, 35 (1933).

⁶ K. Wieland, *Nature* **130**, 847 (1932).

⁷ W. W. Watson and A. E. Parker, *Phys. Rev.* **37**, 1484 (1931).

⁸ A. K. Dutta, *Acad. Sci. U. P. India Bull.* **1**, 89 (1931–32).

** A level of a molecule with three normal modes of vibration must be identified by three quantum numbers. These will be given in the order ν_1 , ν_2 , ν_3 , and that they belong to the excited or normal electronic state will be indicated by the prime and double prime, respectively.

¹ H. A. Stuart, *Zeits. f. Physik.* **59**, 13 (1929).

² D. M. Dennison, *Rev. Mod. Phys.* **3**, 180 (1931).

³ For references see H. A. Stuart, *Molekulstruktur*, Springer, 1934.

graphs at various pressures, and a new analysis of the system is here proposed.

The present analysis has been facilitated by several recent developments. For one thing, the intensity problem for electronic-vibrational bands of the XY_2 type of molecule has been attacked by consideration of the extended Franck-Condon principle in the case of chlorine dioxide by Urey and Johnston⁹ and recently by Ku.¹⁰ Also, applications of the group theory¹¹ have led to the formulation of vibrational and electronic selection rules.

EXPERIMENTAL

Absorption spectra were taken with various tube lengths from 40 cm to 4 meters and pressures between 1 mm and 60 cm of mercury. A 40 cm tube with 1 mm pressure brought out the bands in the region 2900Å while the 4 meter tube with 60 cm pressure was required for bands at 3900Å. This intensity factor of several thousand necessitated the taking of a large number of plates. The light source was a continuous hydrogen discharge for the shorter wavelengths and a tungsten filament lamp in the longer wavelength region where the lines in the hydrogen source became troublesome. Many comparison pictures with the gas at two temperatures were taken in order to be able to assign with some assurance the lower vibrational states involved in the various transitions (see below). The temperature differences were usually about 40°C, spaced about room temperature, although some plates for ranges from -80°C to 600°C were taken. The instrument used was a Hilger E3 spectrograph which was well suited to the examination of the vibrational structure, inasmuch as plates taken in the first order of the 21-foot grating showed resolution insufficient to be of additional help.

On the plates the bands obtained were so broad as to render wavelength determinations with a comparator in the usual way liable to considerable error unless many re-settings were made. To avoid this necessity, the measurements

were taken from microphotometer traces, which shaped the bands and further showed up "satellite peaks" difficult to measure directly. The traces gave also the comparison of intensities required for temperature variation information. In the absence of sharp edges, wavelength determinations were made of the points of maximum absorption for each peak. Lines or the edges of opaque paper strips gummed on the plate were used as reference marks, and the intervals between them were calibrated from the iron comparison spectrum by comparator measurements. The absorption peaks measured with a scale from the reference marks on the trace were then located on the calibration "distance-wavelength" chart. Such a graph was made for each plate as the dispersion was never exactly repeated in two exposures. A large number of plates under various conditions of exposure were measured and the frequencies taken from weighted averages; except where noted each value comes from three or more plates. The uncertainty with this procedure arises from averaging values for peaks resolved on one plate with values for the same peaks only partially resolved on other plates taken under slightly different pressures. However the values were consistent within about 15 cm⁻¹.

INTENSITY AND TEMPERATURE VARIATION

The use of the microphotometer as applied to the measurement of intensity changes with temperature in temperature variation of absorption spectra is discussed in the preceding paper.¹² Some of the complications encountered in practice have been more fully considered there. These may be summarized as unresolved rotational structure, overlapping of vibrational bands and the background of absorption arising from many weak bands. In spite of these embarrassments, temperature variation gave valuable clues to an arrangement of the band system.

In a gas whose molecules have only non-degenerate vibrational energy levels, the molecules are distributed among the latter according to the Boltzmann law $N_G = N_0 e^{-G''/hc/kT}$. A temperature difference of 40°C is ample to show pronounced changes in intensities of absorption for bands in the spectrum of SO₂ coming from

⁹ H. C. Urey and H. Johnston, *Phys. Rev.* **38**, 2131 (1931).

¹⁰ Z. W. Ku, *Phys. Rev.* **44**, 376 (1933); **44**, 383 (1933).

¹¹ R. S. Mulliken, *Phys. Rev.* **43**, 279 (1933); L. Tisza, *Zeits. f. Physik* **82**, 48 (1933); A. V. Bushkovitch, *Phys. Rev.* **45**, 545 (1934).

¹² J. H. Clements, *Phys. Rev.* **47**, 220 (1935).

TABLE I. Observed bands.

ν	Intensity	$(G_b - G_a)''$ from Temp. Var.	ν	Intensity	$(G_b - G_a)''$ from Temp. Var.	ν	Intensity	$(G_b - G_a)''$ from Temp. Var.	ν	Intensity	$(G_b - G_a)''$ from Temp. Var.
25188	0.02		29832	.9	0	31567	60		35168	800	0
25733	.1	230	29896	.9	500	31607†			35297 R	1500	
26109	.2	140	29946	1.4	0 ←	31646	120	(4) 500	35390		
26253°			29967	1.2	500	31719	100		35474 S	1200	
26469	.1	220	29994	1.2	1000	31767	80		35507 T	1200	
26609°			30048	1.2	(2) 1000	31793†			35532°		
26672	.3	60	30076	1.5	0	31858	90		35634	300	
27005	.4	0 ←	30103	1.6	0	31926	200	200	35682	700	
27355	.1	120	30139	3.0	0	31945 A*		0† ← (5)	35742 U	1500	
27510	.2	200	30185	2	500	32161 B†	300		35839 V	1200	
27594	.2	300	30267	3	150	32377 C	600		35960 W	1000	
27940	.2	250	30343†			32607 D	800		36064 X	600	
28200†			30368	6	300	32850 E	1200		36153 Y	600	
28296	.3	200	30394†			33080 F	1700		36241°	200	
28466	.1	400	30432†			33313 G	2000		36292	500	
28514	.1	400	30500	8	200	33547 H	1900		36337	600	
28588	.2	550	30582	10	70	33760 J	2000		36381	600	
28604°	.2		30675	15	50	33960 K	1700		36511	500	
28802†			30700†			34030 L	1600		36558	800	
28818	.2	150	30721°	20	0 ←	34180 M	1600		36653	200	
28910°			30779†		(3)	34200 M'	1600		36707		
29036	.3	400	30801†			34241	700		36761		
29095	.2	400	30855	25	60	34396 N	1600		36875		
29223	.2	470	30895†			34462 N'	900		36937		
29300	.2		30970	40	40	34488	400		37015		
29403	.2	400	30985†			34620 O	1700		37135		
29447	.3	200	31028	40	40	34698	400		37233	600	
29472°			31065°			34724	200		37358		
29522	.3		31124	40	0	34785	1000		37442		
29622	.3		31241†			34846 P	1600		37560		
29656	.5		31280†			34940°	100		37682		
29692	.6		31330	50	0	34970	500		37773	300	
29742	.8		31360†			35053 Q	1800		37810		
29798†			31427	60	500	35133°			37900		
			31507	65							

° Indicates that the measurement is considered less reliable than the others. In most cases it comes from fewer than three plates but in others the overlapping of bands gives rise to the uncertainty.

°° From this point the bands tend to become diffuse.

† Values taken from Watson and Parker's tables.⁷ Bands not observed or not sufficiently resolved for measurement on the present writer's plates. These fit in the proposed scheme as originating from excited vibrational states and so would show more prominently on plates taken at temperatures higher than have been used here.

* Value taken from Lotmar's¹³ series. Not clearly resolved on the present writer's plates.

† The letters correspond to those identifying the peaks in the reproduced microphotometer trace.

The brackets embrace the bands considered in the various temperature variation groups. For each group the arbitrarily selected fiducial band is indicated ←. (See text). For bands to the higher frequency side of † no significant variation with temperature was found.

different initial levels. With any given tube length and pressure only a small group of bands out of the whole system appears favorably. Hence selecting an arbitrary band (a), the difference between the initial level of any other band (b) of the group and that of the selected band (a) is given by the relation:

$$\log_{10} (\rho_b / \rho_a)$$

$$= -0.623(1/T_2 - 1/T_1)(G_b - G_a)'', \quad (1)$$

where the G 's are vibrational term values in cm^{-1} and ρ_b / ρ_a is the ratio on the traces of the heights of absorption peaks under examination above the line of zero absorption for the two temperatures.¹² The relation is valid only for small absorptions and a not overexposed continuous background.

As seen in Table I, temperature variation was considered in the five bracketed groups; for each group the arbitrarily selected fiducial band is indicated. To obtain reliable estimates of $(G_b - G_a)''$ it is important that the intensity

range be not too great. The breaks between the groups are associated with somewhat sudden changes in the intensities, so that to relate the lower levels of the selected bands with overlapping spectrum photographs would require temperature variation comparison beyond the limits imposed in developing Eq. (1). Moreover very little confidence can be placed in the data obtained by comparing temperature variations of a band appearing at the end of one group and appearing at the beginning of the next. For in the first group the band appears with high and in the other with low intensity inasmuch as the exposure times for the two photographs are different.

For the group (4) just to the red of that showing no significant variation with temperature, the equation:

$$\log_{10} \rho_b = -0.623(1/T_2 - 1/T_1)G_b'' \quad (2)$$

¹³ W. Lotmar, Zeits. f. Physik **83**, 765 (1933).

was used to determine directly the term values G_b'' involved. This equation is developed in the same way as Eq. (1), except that the approximation $N_0^{(T_1)} = N_0^{(T_2)}$ is made for the small temperature change. Two of the stronger absorptions showed $G_b'' = 500 \text{ cm}^{-1}$, so these were assigned as coming from $(0, 1, 0)''$.

An analysis of the band system must yield an arrangement in which the frequencies in the energy level diagram, the intensities of the transitions and the temperature behavior of the bands are consistent. The vibrational levels of the normal state are known to be spaced approximately according to multiples of 500 and 1100 cm^{-1} . If for a certain peak $(G_b - G_a)''$ comes out not a multiple of 500 or 1100 but as an intermediate value when an observed ρ_b/ρ_a is substituted in Eq. (1), it may be assigned to a suitable combination of overlapping components. For example, peak *A* (see microphotometer trace Fig. 1) gives $(G_b - G_a)''$ as 200 cm^{-1} , which has been interpreted (see Table III) as a not too close overlapping of transitions from $(0, 0, 0)''$, $(0, 3, 0)''$, and $(1, 0, 0)''$; further overlapping components are thought to be weak. When two bands, whose spectral frequencies suggest that they be assigned as coming from the same lower level, show a small difference in temperature behavior, it is assumed that one of them is composite and it is assigned a second time in the matrix diagram of bands in the place that this difference and the intensity seem to warrant.

THEORY

Any organization of the data must conform to the following theoretical demands.

(a) Group Theory¹¹

The normal electronic state of this molecule of symmetry type C_{2v} may be safely assumed to be of type 1A_1 , since SO_2 gas is diamagnetic. The excited electron state may then be A_1 , B_1 or B_2 , since only A_2 is forbidden to combine with A_1 according to electronic selection rules; however, weak transitions even to A_2 are possible if allowed by electronic $\times$ vibrational selection rules.¹⁴ The normal modes of vibration ν_1 , ν_2 and all resulting

vibrational levels are of type a_1 , while ν_3 is of type a_1 for ν_3 even and b_2 for ν_3 odd. The types of allowed transition will be summarized in tabular form taking the lower electronic state to be of type A_1 . It will be noted that the capital letters refer to electronic types while the small letters are used to denote vibrational types. The absorption should be strong when both the electronic types and resultant electronic $\times$ vibration types are permitted by the group theory selection rules to combine. All selection rules developed will be strict even in the region of large vibrational quantum numbers, for the correction terms added to the representations of the vibrational motion to admit finite amplitudes must be of the same symmetry as those of the main term.

TABLE II. Allowed transitions. Lower electronic state A_1 .
 ν_3'' even ν_3'' odd

Upper electron state	ν_3'' even	ν_3' odd	ν_3' even	ν_3' odd
A_1	z	y	y	z
A_2	—	(x)	(x)	—
B_1	x	—	—	x
B_2	y	z	z	y

The letter indicates the direction of vibration associated with the electric moment in the transition; z is the symmetry axis passing through the sulphur atom in the plane of the molecule, while x is the axis at right angles to this plane. The bracket indicates that the electronic change is forbidden.

If the configuration of the molecule in the normal state is an obtuse angled triangle,³ the moments of inertia lie $I_x > I_z > I_y$, and remain in this order for apex angle 70 – 180° , so that the band structures should show differences for (y) and (z). An investigation of the rotational structure under high dispersion would be necessary to show the type of excited electronic state present.

(b)

In accordance with the Franck-Condon principle the two symmetrical frequencies would be expected to appear with greater or less intensity depending on the forms of ν_1 and ν_2 and the configuration of the molecule in the excited state. If the S—O force is approximately central in nature and the S—O distance does not change very greatly during the electronic transition, the value of ν_1' should be of the same order of magnitude as ν_1'' . A series with frequency differences

¹⁴ G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

very much less than this would then undoubtedly be a ν_2' progression.

LOWER FREQUENCY BANDS

The temperature variation method points to a weak band at about $31,950\text{ cm}^{-1}$ as most probably the $(0, 0, 0)'' - (0, 0, 0)'$ transition. However, other possibilities not convincingly ruled out on this score were tried as origin. The choice of $31,945\text{ cm}^{-1}$ gave a scheme so much more consistent and in accord with intensity and temperature behavior data that there can be

little doubt of its correctness. Further, the fact that it fits in with a simple-appearing series of increasing intensity lends the assignment strong support.

On the basis of this assignment of origin, vibrational quantum numbers have been assigned for a large number of the prominent bands. These are given in the form of a matrix (Table III). The averages of the differences $\Delta G_2''$ between the ν_2'' levels as taken from this table run 520 cm^{-1} , 525 , 529 , 530 , 524 , 522 , 511 , 526 , 507 cm^{-1} , the latter two values appearing from only two

TABLE III. Lower frequency bands.

$\frac{(\nu_1\nu_2\nu_3)'}{(\nu_1\nu_2\nu_3)''}$	000	010	020	030	040	050	060	070	080	090	Av.									
000	31945 518	216 515	32161 519	216 519	32377 519	230 519	32607 519	243 519	32850 519	230 519	33088 519	225 519	33313 519	234 519	33547 519	213 519	33760 519	230 519	33990 519	518
010	31427 532	219 522	31646 522	212 528	31858 528	Masked by strong (ono)' progression														527
020	30895* 527	229 542	31124 542	206 529	31330 529	237 528	31567 521	234 521	31801* 521											529
030	30368 534	214 534	30582 534	219 539	30801* 539	238 539	31029 539	241 539	31280 539	227 537	31507 537	212 537	31719 537	226 518	31945 518					534
040	29832 532	216 526	30048 526	219 522	30267 522	233 533	30500 533	241 533	30741 533	229 538	30970 538				31427 532					530
050	29300 498	222 498	39522 498	220 519	29742 519	225 521	29967 521				30432* 536	243 536	30675 536	220 536	30895* 518					522
060	28802* 506				29223 506	223 536	29446 536	246 536	29692 536	204 536	29896 493	243 493	30139 518							513
070	28296						28910				29403	218	29621* 526							526
080													29095 507							507
090													28588 507	230 507	28818 518	218 518	29036 518	230 518		
Av.		219		215		231		241		223		228		226		216		230		
100	30801* 534	227 534	31028 528	213 528	31241* 520				31707 520	219 520	31926 499	235 499	32161 515	216 515	32377 519	230 519	32607 519	243 519	32850 519	519
110	30267 525	233 525	30500 533	221 533	30721 536	240 536	30961 529				31427 532	219 532	31646 522	212 522	31858 498					525
120	29742 519	225 520	29967 520	218 520	30185 529	247 529	30432* 536	243 536	30675 536	220 536	30895* 527	229 527	31124 542	236 542	31360* 506	207 506	31567 506	200 506	31767 506	530
130	29223 519	224 519	29447 519	209 519	29656 522	240 522	29896 522	243 522	30139 522	229 522	30368 522	214 522	30582 522							526
140											29822 522	254 522	30076 522							522
150											29300									
Av.		227		215		242		243		223		230		221		218		221		
200	29621* 532	211 532	29832 532	216 532	30048 526	219 526	30267 525	233 525	30500 506	241 506	30741 506	229 506	30970 538							525
210			29300 498	222 498	29522 506	220 506	29742 522	252 522	29994 522				30432* 536			30855 536	210 536	31065 536		519
220	28588 506	214 506	28802 506						29472 522	220 522	29692 522	204 522	29896 522	207 522	30103 541					524
230			28296												29562 526	236 526	29798* 526			526
240	27510 505										28604 522	214 522	28818 522	218 522	29036 522					514
250	27005 536												28296 536	218 536	28514 536					536
260	26469																			
Av.		213		219		220		242		230		216		214		236		210		
500	26253 520	216 520	26469 520	203 520	26672 520															520
510	25733 545																			545
520	25188																			
Grand Average		220		215		232		242		224		226		219		226		221		

Nine other observed frequencies have been fitted into the scheme in scattered places conforming with the general parabolic arrangement of intensity.

* indicates a value taken from Watson and Parker's data.⁷

pairs of bands. These may be summarized by the equation

$$G_2'' = 516.4\nu_2'' + 4\nu_2''^2 - 0.4\nu_2''^3.$$

The occurrence of series in which the ΔG 's first increase, then decrease, is not unusual in polyatomic molecules.⁹ For ν_1'' , the ΔG 's obtained vary more widely, being 1144 cm^{-1} , 1195, 1157, 1111, 1102 cm^{-1} ; they follow the formula

$$G_1'' = 1086\nu_1'' + 70\nu_1''^2 - 13\nu_1''^3.$$

The unsymmetrical frequency known in the normal state, $\nu_3'' = 1360 \text{ cm}^{-1}$, has not been mentioned in the tabular analysis. Since the band system is of considerable intensity the possibility of the excited state being of type A_2 is excluded, and the $(\nu_3'' = 0, \nu_3' = 0)$ quantum jump should appear in the spectrum. Unless $\nu_3' \approx \nu_3''$, in which case $\Delta\nu_3 = 0$ is the most probable transition, transitions from excited unsymmetrical levels are to be expected among the lower frequency bands. The small frequency (see later) makes it probable that such bands are masked by overlapping; that is, if $(\nu_3'' - \nu_3')$ are approximately multiples of 225 cm^{-1} , the symmetrical and unsymmetrical progressions lie superposed. In an arrangement of the band system it would have been plausible to have assumed, for example, band 30,801 cm^{-1} as $(0, 0, 1)'' - (0, 0, 1)'$. However in view of the fact that the electronic type of the excited state, hence the selection rule for transition between unsymmetrical term values (see Table II), is unknown, any assignment in this way was felt would be purely arbitrary. The data for the vibrational levels of the normal state are collected in Table IV.

Table IV is of interest particularly with regard to the ν_2'' series. Lotmar's values from fluorescence have very small second differences, and that the differences obtained by other workers show variation may perhaps be accounted for on the basis of band structure. It will be noted that Chow's emission values decrease with increasing quantum number, while the values in absorption run larger. That is, in emission we must say that the point of maximum intensity in the rotation band is distant from its origin by an amount which varies from band to band. In absorption the point of maximum absorption

TABLE IV. *Vibrational levels of the normal state.*

	Level	Infrared ³	Chow ¹⁵	Lotmar ¹⁵	Jonescu†	Present writer
ν_1''	0	0	0	0	0	0
	1	1152	1150 (A)	1150	(1144)	1144
	2		2300 (A)	2300	(2270)	2339
	3		3450	3450	(3378)	3496
	4		4600	4600	(4468)	4607
	5			5750	(5540)	5709
	6			6900		
ν_2''	0	0	0	0	0	0
	1	525	521	520	(530)	520
	2		1043	1040	(1060)	1045
	3		1553 (A)	1560	(1590)	1574
	4		2069	2075	(2120)	2104
	5		2578	2590	(2560)	2638
	6		3086	3110	(3180)	3150
	7		3590	3630	(3710)	3661
ν_3''	0	0	0	0	0	0
	1	1361	1354?	1370	(1360)	
	2		2676?	2720	(2702)	
	3		3966?	4060	(4024)	

† Computed from the Deslandres' formulae given.

should also vary, only in this case the variation might be in the opposite direction.

HIGHER FREQUENCY BANDS

While the bands on the lower frequency side of the origin fall into the matrices shown in Table III, those on the higher frequency side, with the exception of the first eight members, present a confused and irregular appearance (see Fig. 1—sample microphotometer trace). Since the frequencies cannot be made to follow regular progressions, partly because the values are taken for the points of maximum absorption in each band, but perhaps mainly because of some inherent disturbances in the levels of the upper state, the microphotometer trace was examined for clues to an organization. It will be seen in Fig. 1 that the intensity increases to peak G, then follows a plateau of intense peaks, after which comes a somewhat regular decrease of intensity in the neighborhood of V. Finally appears a region of collision predissociation about 2600A, which has been explained as pressure broadening due to an influence of the existence of neighboring electron states.¹⁶ This predissociation occurs only when selection rules are broken down by collision. The perturbing influence of the discrete levels of these same, or other, states may perhaps

¹⁵ The summary of Chow and Lotmar's values is taken from H. D. Smyth, *Phys. Rev.* **44**, 690 (1933).

¹⁶ J. Franck, H. Sponer and E. Teller, *Zeits. f. physik. Chemie* **B18**, 88 (1932).

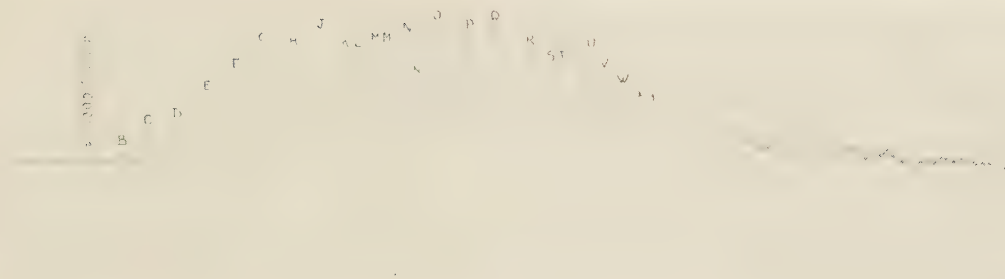


FIG. 1. Microphotometer trace of higher frequency bands. (Many lower frequency bands appear to the left of $(0, 0, 0)'' - (0, 0, 0)'$ with larger numbers of molecules in the absorption path.)

be invoked to explain the irregularities among the lower frequency bands.

The plateau of intensity suggests the overlapping of a number of series of about equal intensities. In looking for the beginning of the $(1, v_2, 0)'$ progression the double peak *KL* is first arresting; but that the doubling indicates the first member of this progression is little likely in that the frequency interval, 2045 cm^{-1} , is somewhat larger than expected. Also the unsymmetrical appearance of peak *H* argues that the new series begins at lower frequency. Particularly striking also is the intense band *O* which is apparently rather free of satellite peaks. The appearance of the fairly intense peak *V*, obviously in a new series without distinct previous members, is also interesting. These observations have led to the placing of the beginning of the new progression at *G* (see Table V).

As in the series beginning with *A*, the intensity may be assumed to rise slowly, *G* being affected negligibly, *H* and *J* with increasing influence with the maximum of intensity at the sixth member *O*, corresponding to the most intense sixth member *G* in the $(0, v_2, 0)'$ sequence. If this has been correctly placed, the $(2, v_2, 0)'$ progression begins with *O* and the $(3, v_2, 0)'$ progression with *V*. The v_1' levels on this analysis converge rapidly and there is obviously some disturbance in the spectrum at peak *O* (indicated by the line drawn in Table V), which, however, is to be expected in any organization in view of the different appearance of satellites in the bands on the two sides of *O*. Perhaps this is due to an interaction of the normal modes of vibration in the upper states, and since v_1 , v_2 and even multiples of v_3 belong to the same representation of

the symmetry group, such an interaction is not improbable. If this is the case, the scheme drawn up is simply an attempt to approximately separate v_1' and v_2' . With increasing amplitudes of vibration of the molecule corresponding to the higher vibrational quantum numbers, the interaction may be supposed to increase, and that a sudden increase in coupling might occur in the upper state corresponding to the energy $A - O$, should not be regarded as too strange.

The apparent disturbance at *O* in Table V may be explained perhaps more satisfactorily on the basis of a sharp decrease of intensity in the $(1, v_2, 0)'$ progression at $v_2' = 6$. Such intensity irregularities are known in the spectra of diatomic molecules.¹⁷ If this is the case here, the bands

TABLE V. Proposed transitions from $(0, 0, 0)''$.

	$(0, v_2, 0)'$		$(1, v_2, 0)'$		$(2, v_2, 0)'$		$(3, v_2, 0)'$
$v_2' = 0$	A 31945 216	1368	G 33313 217	1307	O 34620 226	1219	V 35839 225
1	B 32161 216	1369	H 33530 230	1316	P 34846 207	1218	X 36064 228
2	C 32377 230	1383	J 33760 235	1293	Q 35053 244	1239	36292 219
3	D 32607 243	1388	KL 33995 220	1302	R 35297 198	1214	36511 196
4	E 32850 230	1365	MM' 34215 225	1280	ST 35495 247	1212	36707 230
5	F 33080 233	1360	NN' 34440 180	1302	V 35742 218	1195	36937 198
6	G 33313 234	1307	O 34620 226	1340	W 35960 198	1175	37135 223
7	H 33547 213	1299	P 34846 207	1307	Y 36158 223	1200	37358 202
8	J 33760 235	1293	Q 35053 244	1328	36381 244	1179	37560
9	KL 33995 220	1302	R 35297 198				
10	MM' 34215 247	1280	ST 35495 247				
11	NN' 34462 236	1280	V 35742 218				
12	34698	1262	W 35960				

In this table $\Delta v_2'$ differences are shown horizontally and the $\Delta v_1'$ differences vertically. The break in the frequency differences at *O* is discussed in the text.

¹⁷ For example, R. W. Wood and F. W. Loomis, Phil. Mag. **6**, 231 (1928); I_2 fluorescence. R. S. Mulliken, Phys. Rev. **25**, 259 (1925); BO.

below the line in $(1, v_2, 0)'$ are wrongly assigned, and since peak O is without a strong satellite where $(1, 6, 0)'$ should appear, the bands O, P, Q , should be placed as belonging to the $(2, v_2, 0)'$ progression alone. That this is the more plausible assignment is substantiated by the fact that peak $V, (3, 0, 0)'$, is much the strongest member of the $(3, v_2, 0)'$ progression, and thus the $(2, v_2, 0)'$ progression may well have a first member with relatively high transition probability.

The first few v_2' levels should in any case not be of mixed type and their intervals appear in Table III. These levels may be represented by the formula

$$G_2' = 219v_2' + 1.0v_2'^2 + 0.5v_2'^3,$$

which however fails to take into account the small decrease in the difference between the second and third levels. The v_2' frequency difference, approximately 225 cm^{-1} , as already noted by Lowater¹⁸ is prominent throughout the band system. The v_1' levels, if the assignment of bands just given is correct, may be approximately summarized

$$G_1' = 1373v_1'^2 - 7v_1'^3 - 6v_1'^4.$$

No bands corresponding to transitions from excited vibrational levels of the normal state to levels of the excited state involving v_1' greater than zero have been assigned. In view of the coincidence $v_3'' = v_1'' + v_2'$ and the approximate coincidences $v_3'' \approx 6v_2'$, $v_1'' \approx 5v_2'$, together with the uncertainties in the frequencies due to overlapping, such a definite assignment of satellite peaks does not seem justified. No significant temperature variation of these satellite peaks has been observed; this would indicate that these are weak if this interpretation of them is correct. $(1, 0, 0)'' - (1, v_2, 0)'$ might show most favorably through temperature changes among the weaker bands near the origin, but it is believed that the transition probability of these in this region is small.

The double bands KL, MM' and ST with reduced intensity as compared with adjoining peaks are of interest. The doubling may be ascribed to a resonance splitting of the level due

to another level in close proximity, in which case the intensity of transition would be shared. Against this assumption is the apparent absence of splitting in the neighboring levels which should also be favorably placed to show the effect. Another peculiar feature of the spectrum is the slight alternation of intensity shown in the bands $A-J$. This at first suggested two progressions, but if so, the two progressions could not converge to the same point. No reasonable explanation of the phenomenon has been found.

CONFIGURATIONS AND FORCE CONSTANTS OF THE SO_2 MOLECULE

From infrared investigations Bailey and Cassie¹⁹ conclude that the normal apex angle is 122° although their valence force assumption permits both a 60° and a 120° solution. This conclusion rests on the identification of the 1360 cm^{-1} frequency as the unsymmetrical one. In the analogous molecule, ClO_2 , Ku¹⁰ on the other hand favors the acute angled form.

Van Vleck and Cross²⁰ have developed a valence force solution for this type of molecule, which on a present calculation leads to values of the force constants $(\text{S}-\text{O}) = 9.8 \cdot 10^5$ and $(\text{O}-\text{O}) = 0.42 \cdot 10^5$ dynes/cm. Here the cross terms in the potential energy expression are neglected, although if the $(\text{O}-\text{O})$ force is partly central in character for SO_2 these may be of importance. However a purely central force assumption does not give a solution for the frequencies observed. The $\text{S}-\text{O}$ distance used in the present calculation is that obtained by Wierl²¹ from electron diffraction, *viz.*, 1.37A. From crystal structure data the $\text{S}-\text{O}$ distance corresponding to a single bond should be about 1.50A, while that corresponding to a double bond should be about 1.35A. If one of the bonds is single and the other double the resultant value should be closer to the double bond distance due to the exchange energy.*

¹⁹ C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. London **A140**, 605 (1932).

²⁰ J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

²¹ W. Wierl, Phys. Zeits. **31**, 1028 (1930).

* My thanks are due to Professor Zachariasen of this department for a discussion on this point. In his opinion also the apex angle should not be greatly different from the tetrahedral angle 125° .

¹⁸ F. Lowater, Astrophys. J. **31**, 311 (1910).

If the molecule is in the normal state when it absorbs the incident light, then the transition will be strongest to the excited state for which the end-point of the vibrational motion (i.e., all the vibrational energy potential) puts the molecule in the configuration most nearly that of the normal state. The intensities in Fig. 1 and the proposed arrangement in Table V show there is no single band that may be definitely taken to be the most probable transition from $(0, 0, 0)''$. The probabilities of transition of $(v_1'' - v_1')$ and $(v_2'' - v_2')$ (to the extent that these may be considered unmixed ν_1 and ν_2 in the two electronic states) in combination cause a number of bands to appear with about the same intensity. If the intensity explanation of the disturbance at peak *O* is accepted, a parabola of maximum intensities can be drawn in Table V. Selecting a central value on this parabola, the excited molecule vibrating with $v_1' = 1$, $v_2' = 3$, $v_3' = 0$ may be taken as having vibrational energy potential sufficient to put the molecule in the configuration of the vibrationless normal state. The energy difference $(1, 3, 0)' - (0, 0, 0)'$ is $2050 \cdot \text{cm}^{-1}$ (0.25 volt). Since the S—O distance and the OSO angle both

undoubtedly change from their values in the normal electronic state, it is not possible from this data to determine the shape and dimensions of the molecule in the excited state.

Jonescu²² from a partial rotational analysis reports the OSO angle in the excited state as 96° . With the frequencies 225 cm^{-1} and 1370 cm^{-1} recognized in the spectrum, Eq. (4) of Bailey and Cassie²³ was used to suggest a possible ν_3' frequency. The solutions are in the neighborhood of 1400 and 250 cm^{-1} ; the former involving the less change from the unsymmetrical frequency in the normal state appears the more likely. If then the unsymmetrical frequencies in the two states are so nearly equal it is not surprising (see discussion earlier) that these were not identified in the spectrum.

The writer wishes to thank Professor R. S. Mulliken for the suggestion of the problem and for much help and encouragement throughout the investigation.

²² A. Jonescu, *Comptes rendus* **196**, 1476 (1933).

²³ C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc. London* **A137**, 630 (1932).

